

## THE CRYSTAL AND MOLECULAR STRUCTURE OF $\pi$ -CYCLO- HEPTATRIENYLIUMTRICARBONYLMOLYBDENUM(0) TETRAFLUOROBORATE

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### SUMMARY

The crystal and molecular structure of  $\pi$ -cycloheptatrienyliumtricarbonylmolybdenum(0) tetrafluoroborate has been determined using X-ray diffraction techniques. The orange crystals are orthorhombic, space group *Pbca*. The unit cell dimensions are  $a = 16.297(2)$ ,  $b = 12.955(2)$  and  $c = 11.749(2)$  Å and with eight molecules per cell, the calculated density is  $1.91 \text{ g/cm}^3$  versus  $1.90 \text{ g/cm}^3$  measured by flotation. The structure was solved by the heavy atom method and refined by full-matrix least-squares method to a final *R* of 0.049 for the 1383 observed reflections used in the analysis. The cation has a 'piano stool' arrangement, with the planar cycloheptatrienylium ring as a 'seat' and the three carbonyl groups as 'legs'. While the average C-C distance in the  $\text{C}_7\text{H}_7^+$  ring of 1.400 Å is similar to that found in other  $\text{C}_7\text{H}_7^+$  ring systems, the average Mo-C(carbonyl) distance of 2.032 Å is longer than that found in other molybdenum tricarbonyl complexes.

### INTRODUCTION

In comparison to the extensive structural investigations of  $\pi$ -cyclopentadienyl complexes, the  $\pi$ -cycloheptatrienyl ligand has been virtually ignored. Only two preliminary reports on  $\pi$ -cycloheptatrienyl complexes,  $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ <sup>1</sup> and  $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)^2$ , had appeared when we initiated our study of  $\pi$ -cycloheptatrienyliumtricarbonylmolybdenum(0) tetrafluoroborate and only one other structural study has appeared  $(\pi\text{-C}_7\text{H}_7)(\sigma\text{-C}_6\text{F}_5)\text{Mo}(\text{CO})_2$ <sup>3</sup> since our preliminary report<sup>4</sup>. We were interested in the nature of the interaction of the metal atom with the formally positive  $\text{C}_7\text{H}_7$  ring as compared to the anionic  $\text{C}_5\text{H}_5$  system. Our results have indicated that a stronger interaction exists between the  $\text{C}_7\text{H}_7$  ring and the  $\text{Mo}(\text{CO})_3$  group as indicated by the longer Mo-C(to CO) distances than are usually found in  $\text{Mo}(\text{CO})_3$  complexes.

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## EXPERIMENTAL

*Unit cell and collection of intensity data*

The method given by King<sup>5</sup> was used to prepare  $\pi$ -cycloheptatrienylium-tricarbonylmolybdenum(0) tetrafluoroborate. Preliminary Weissenberg and precession photographs indicated that the orange crystals were orthorhombic; the systematic absences of  $0kl$  if  $k=2n+1$ ,  $h0l$  if  $l=2n+1$  and  $hk0$  if  $h=2n+1$  uniquely determined the space group to be *Pbca* (No. 61).

A small crystal of dimensions  $0.10 \times 0.09 \times 0.05$  mm was mounted with the  $c$  axis parallel to the  $\varphi$  axis of a single crystal orienter mounted on a General Electric XRD-6 automated diffractometer. The unit cell dimensions were obtained from a least-squares treatment of the  $2\theta$  values for 17 Cu- $K_\beta$  ( $\lambda$  1.39217 Å) diffraction maxima. The final values are  $a=16.297(2)$ ,  $b=12.955(2)$  and  $c=11.749(1)$  Å. The density calculated for eight molecules of  $C_7H_7Mo(CO)_3BF_4$  per unit cell is  $1.91$  g/cm<sup>3</sup> compared to  $1.90$  g/cm<sup>3</sup> measured by flotation in a  $CCl_4/CH_2I_2$  mixture.

The intensity measurements were made using the stationary-crystal-stationary-counter method with Cu- $K_\alpha$  ( $\lambda$  1.54051 Å) radiation. A 20 sec count was taken for all the reflections with  $2\theta \leq 135^\circ$ . A total of 9104 measurements was made, giving at least 3 and sometimes 4 measurements of each independent reflection. After averaging equivalent reflections, a total of 1392 reflections which were greater than 1.2 times their respective background were considered as observed and used in the analysis. An additional 842 reflections were considered unobserved and flagged with a minus sign. Four standard reflections were remeasured after every 100 measurements and their variations (3%) were approximately those associated with the counting statistics. A correction for the  $\alpha_1$ - $\alpha_2$  splitting at high  $2\theta$  values was applied and the data reduced to a set of structure amplitudes in the usual manner. The absorption coefficient is  $97.8$  cm<sup>-1</sup> but no corrections to the intensities were made because of the small size of the crystal. In addition, there was only a small variation ( $\pm 10\%$ ) in the intensity when the crystal was rotated about  $\varphi$  at  $\chi=90^\circ$ .

## SOLUTION AND REFINEMENT OF THE STRUCTURE

A sharpened Patterson function indicated that the  $z$  parameter for the molybdenum atom was approximately  $\frac{1}{4}$ , giving rise to an ambiguity in the  $x$  parameter between  $x$  and  $\frac{1}{4}-x$ . A Fourier synthesis calculated using phases based only on the molybdenum atom can not distinguish between these two possibilities, since the two Fourier syntheses would be identical except for the operation of  $\frac{1}{4}-x$ . Therefore, a Fourier synthesis was calculated on the basis of only the molybdenum atom and the majority of the light atoms in the cation were located. Then, two structure factor Fourier syntheses were calculated, first with all the atoms at positions  $x,y,z$  and the second with all the atoms at  $\frac{1}{4}-x,y,z$ . The  $BF_4^-$  ion was ill-defined (as anticipated) in both electron-density maps but the position which gave the lower  $R$  value was deemed correct and approximate positions for the fluorine atoms in the  $BF_4^-$  ion were calculated. When a model assuming two sets of half-weight fluorine atoms refined after 2 least-squares cycles to approximately the same positions as the single fluorine atom model, the latter was retained in all subsequent calculations. The residual  $R$ ,  $R = \Sigma |F_o - |F_c|| / \Sigma |F_o|$ , was 0.10 after 2 least-squares cycles with individual isotropic

thermal parameters. All atoms were converted to their anisotropic equivalent and three full-matrix least-squares cycles reduced  $R$  to 0.053. Although the anisotropic thermal parameters for the fluorine atoms of the  $\text{BF}_4^-$  group are probably not meaningful, this approximation is certainly closer to reality than an isotropically vibrating fluorine atom.

A difference Fourier synthesis was used to locate probable positions for the seven hydrogen atoms on the cycloheptatrienyl cation ring. The contributions of the hydrogen atoms were included in the structure factor calculations for three additional least-squares cycles but their parameters were not varied. The weighting scheme to this point was  $\sqrt{w}=1$  if  $F(\text{low}) \leq F(\text{obs}) \leq F(\text{upper})$ ,  $\sqrt{w}=F(\text{obs})/F(\text{low})$  if  $F(\text{obs}) < F(\text{low})$  and  $\sqrt{w}=F(\text{upper})/F(\text{obs})$  if  $F(\text{obs}) > F(\text{upper})$  where  $F(\text{low})$  was 20.0 and  $F(\text{upper})$  was 180.0. However, for the last three least-squares cycles,  $F(\text{low})=20.0$  and  $F(\text{upper})=80.0$  and the final residual  $R$  was 0.049 for the 1383 reflections used in the refinement. A total of 9 reflections which were near the borderline between observed and unobserved and whose calculated values were less than 2.0 were given zero weight in the refinement. The atomic scattering factors for molybdenum and oxygen were from the usual tabulation<sup>6</sup> while the values for fluorine, carbon and boron were from a more recent calculation<sup>7</sup>. The final positional and thermal parameters are given in Table 1, with the final hydrogen parameters in Table 2.

#### DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The atomic numbering and molecular geometry are illustrated in Fig. 1. The cation has a 'piano stool' arrangement similar to that observed in other  $\pi$ -olefin metal-tricarbonyl complexes. A view down the molybdenum atom-ring-center vector shows the arrangement of the  $\text{Mo}(\text{CO})_3$  group relative to the  $\text{C}_7\text{H}_7$  ring (Fig. 2). The combination of a seven-membered ring with the three-fold symmetry of the  $\text{Mo}(\text{CO})_3$  group does not allow a complete staggering or eclipsing of the ring carbons and the CO groups. Therefore, the observed relationship is not unexpected.

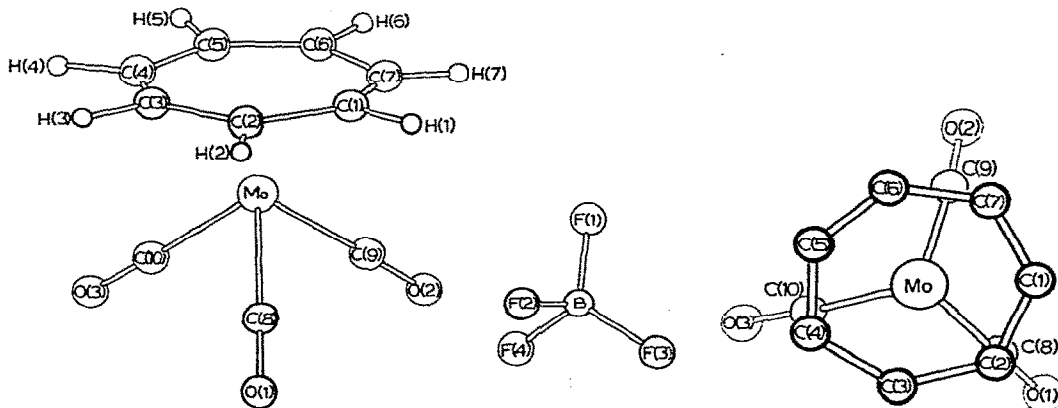


Fig. 1. An arbitrary view of the  $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_3^+$  and  $\text{BF}_4^-$  ions showing the atomic numbering and the overall geometry of the cation.

Fig. 2. The  $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_3^+$  cation as viewed down the ring center to the Mo atom vector, showing the relationship of the  $\text{Mo}(\text{CO})_3$  group to the  $\text{C}_7\text{H}_7$  ring.

TABLE I

## FINAL POSITIONAL AND THERMAL PARAMETERS FOR CYCLOHEPTATRIENYLIUMTRICARBONYLMOLYBDENUM(0) TETRAFLUOROBORATE

The values are  $\times 10^{+4}$ , except for the molybdenum atom which are  $\times 10^{+5}$ . The estimated standard deviations are in parentheses. The temperature factor is of the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}h \cdot k - \beta_{13}h \cdot l - \beta_{23}k \cdot l)$ .

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mo	11273(3)	8811(4)	24888(9)	208(2)	352(4)	538(5)	10(4)	-8(12)	-48(15)
F(1)	3124(7)	862(7)	-40(12)	119(7)	109(8)	344(21)	-112(12)	200(21)	-217(22)
F(2)	2754(10)	2426(13)	-208(21)	179(12)	202(16)	726(50)	-53(27)	-446(42)	350(49)
F(3)	3986(8)	2115(10)	-212(18)	137(9)	165(12)	718(45)	-133(17)	482(36)	-220(40)
F(4)	3240(13)	2018(13)	1156(13)	301(18)	208(17)	194(16)	-260(32)	179(29)	-175(28)
O(1)	1632(6)	3240(5)	2460(12)	100(5)	39(5)	190(12)	-27(8)	-103(18)	14(20)
O(2)	2954(4)	451(7)	3239(9)	28(3)	98(7)	147(10)	9(8)	-22(9)	-9(15)
O(3)	836(7)	1223(9)	5122(7)	100(6)	143(10)	46(7)	16(14)	34(11)	-52(14)
C(1)	1049(8)	676(10)	524(9)	64(6)	86(10)	49(8)	-46(14)	-22(12)	-4(15)
C(2)	363(8)	1251(9)	883(10)	41(5)	60(7)	89(11)	-23(10)	-49(13)	20(15)
C(3)	-192(6)	1012(9)	1749(12)	30(4)	53(8)	142(14)	-14(9)	-32(12)	1(17)
C(4)	-169(5)	199(8)	2505(14)	33(4)	77(7)	112(10)	-21(8)	-18(16)	-69(28)
C(5)	384(6)	-640(7)	2579(13)	42(4)	45(5)	103(10)	-23(7)	-8(17)	8(21)
C(6)	1058(8)	-818(7)	1913(11)	58(6)	33(6)	98(10)	7(10)	-35(13)	-36(13)
C(7)	1382(7)	-236(7)	988(10)	45(5)	66(8)	86(10)	12(10)	5(11)	-69(16)
C(8)	1455(6)	2391(8)	2446(14)	51(4)	53(6)	106(10)	-2(9)	-63(16)	6(24)
C(9)	2315(6)	619(7)	2939(8)	23(4)	56(7)	64(7)	-3(7)	-4(8)	-10(12)
C(10)	941(8)	1127(9)	4177(11)	49(6)	57(9)	92(10)	-14(11)	7(13)	-10(16)
B(1)	3322(9)	1826(10)	130(12)	42(5)	59(9)	67(10)	-16(11)	23(13)	-21(16)

TABLE 2\*

## PROBABLE HYDROGEN ATOM POSITIONS

The hydrogen atom is given followed by the atom to which it is bonded, the position parameters  $\times 10^3$ , the isotropic thermal parameter used in the calculations, and the corresponding C-H distance. *B* is the isotropic thermal parameter for the atom to which the hydrogen atom is bonded.

Atom	Bonded to	x	y	z	<i>B</i> (Å) <sup>2</sup>	Distance (Å)
H(1)	C(1)	139	099	-020	4.5	1.09
H(2)	C(2)	025	196	040	4.0	1.09
H(3)	C(3)	-070	156	188	4.3	1.11
H(4)	C(4)	-067	020	313	4.8	1.09
H(5)	C(5)	026	-121	325	4.5	1.10
H(6)	C(6)	142	-152	211	3.8	1.10
H(7)	C(7)	196	-054	060	4.8	1.11

The  $\text{C}_7\text{H}_7$  ring is planar within experimental error and the equation of the plane defined by the seven carbon atoms is  $0.5640X + 0.5309Y + 0.6325Z = 1.833$ , where *X, Y, Z* are the coordinates in Å. The deviations of the carbon atoms C1-C7 from the plane are  $-0.015, +0.017, -0.015, +0.010, -0.004, -0.002$  and  $+0.007$  Å respectively. Although the displacements are not significant, the atoms C2, C4 and C7 are all displaced towards the carbon atoms of the carbonyl group as if an interaction existed between these atoms. The deviations from planarity in  $\pi$ -complexes is very complicated and is not well understood.

The individual C-C distances in the  $\text{C}_7$  ring range from 1.368 to 1.425 Å with esd of  $\pm 0.017$  Å and an average value of 1.400 Å. The internal C-C-C angles vary from 127 to 130° with an error of  $\pm 1^\circ$  and an average angle of 128.4° (Table 3). The theoretical C-C-C angle for  $D_{7h}$  symmetry would be 128.6°. The C-C distances compare favorably with the values in the two cycloheptatrienyl complexes reported in the literature; 1.40 Å in  $\pi$ -cycloheptatrienyl- $\pi$ -cyclopentadienylvanadium<sup>2</sup> and 1.407 Å in dicarbonyl- $\pi$ -cycloheptatrienyl- $\sigma$ -(pentafluorophenyl)molybdenum<sup>3</sup>. In all cases the  $\text{C}_7$  ring appears as a fully delocalized planar system which interacts with the metal atom in a  $\pi$ -fashion. The molybdenum atom is approximately equidistant from all seven ring atoms, with an average Mo-C distance of 2.314(13) Å and with a range from 2.290 to 2.327 Å and a Mo to ring-plane distance of 1.658 Å. These values are in excellent agreement with the values of 2.316 and 1.659 Å reported for  $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{-C}_6\text{F}_5$ <sup>3</sup>, which suggests a close similarity of the bonding in the two complexes. Churchill and O'Brien<sup>3</sup> have noted that the geometry of metal-arene complexes is dominated by the almost constant metal-ring carbon distances; for example, 2.329 Å in  $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4\text{H}[\text{P}(\text{CH}_3)_2]$ <sup>8</sup>, 2.333 Å in  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7$ <sup>9</sup>, 2.345 Å in  $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ <sup>10</sup>, 2.347 Å in  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCH}_3$ <sup>11</sup>, 2.358 Å in  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{CH}_3]_2$ <sup>12</sup> and 2.374 Å in  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$ <sup>13</sup>. The

\* The Table of structure factors has been deposited as NAPS Document No. 01971, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

TABLE 3

BOND DISTANCES AND BOND ANGLES FOR  $C_7H_7Mo(CO)_3^+BF_4^-$  WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Distance (Å)		Angle (°)	
<i>(a) Involving the C-H<sub>7</sub> group</i>			
C(1)-C(2)	1.408(18)	C(1)-C(2)-C(3)	128(1)
C(2)-C(3)	1.396(17)	C(2)-C(3)-C(4)	128(1)
C(3)-C(4)	1.378(18)	C(3)-C(4)-C(5)	130(1)
C(4)-C(5)	1.415(14)	C(4)-C(5)-C(6)	127(1)
C(5)-C(6)	1.368(17)	C(5)-C(6)-C(7)	130(1)
C(6)-C(7)	1.425(17)	C(6)-C(7)-C(1)	127(1)
C(7)-C(1)	1.409(18)	C(7)-C(1)-C(2)	129(1)
<i>(b) Involving the Mo(CO)<sub>3</sub> group</i>			
Mo-C(1)	2.327(11)	C(8)-Mo-C(9)	85.2(4)
Mo-C(2)	2.311(12)	C(8)-Mo-C(10)	85.0(5)
Mo-C(3)	2.326(11)	C(9)-Mo-C(10)	85.1(4)
Mo-C(4)	2.290(9)	Mo-C(8)-O(1)	178(1)
Mo-C(5)	2.316(10)	Mo-C(9)-O(2)	176(1)
Mo-C(6)	2.306(10)	Mo-C(10)-O(3)	177(1)
Mo-C(7)	2.319(12)		
Mo-C(8)	2.029(10)		
Mo-C(9)	2.036(9)		
Mo-C(10)	2.032(13)		
C(8)-O(1)	1.137(12)		
C(9)-O(2)	1.120(12)		
C(10)-O(3)	1.130(15)		
<i>(c) Involving the BF<sub>4</sub><sup>-</sup> group</i>			
B-F(1)	1.305(16)	F(1)-B-F(2)	111(1)
B-F(2)	1.272(22)	F(1)-B-F(3)	118(1)
B-F(3)	1.213(20)	F(1)-B-F(4)	108(1)
B-F(4)	1.239(20)	F(2)-B-F(3)	111(2)
		F(2)-B-F(4)	96(2)
		F(3)-B-F(4)	111(2)

present value of 2.314 Å is on the low side of these values. The real question is whether the variation in Mo-C(ring) distances from 2.315 to 2.374 Å does not represent varying amounts of interaction between the metal and the ring. In that case the metal-arene distances would not be expected to be constant, as appears to be the case from the available data.

A more interesting observation is the variation in Mo-C(carbonyl) distance as a function of the other groups bonded to the molybdenum atom. A summary of some of these distances is given in Table 4. We see that the replacement of three carbonyls by nitrogen atoms, which are incapable of back-bonding, reduces the Mo-C distance to 1.94 Å<sup>14</sup> from the value of 2.06 Å found in Mo(CO)<sub>6</sub><sup>20</sup>. This decrease in the Mo-C distance is explained on the basis of increased back-bonding in the Mo(CO)<sub>3</sub> case relative to Mo(CO)<sub>6</sub>. However, the value of 2.032(12) Å found in the present study is the longest Mo-C(carbonyl) distance found in a Mo(CO)<sub>3</sub> complex. This observation coupled with the fact that the Mo-C(ring) distance of 2.314(13) Å is one of the

TABLE 4

A SUMMARY OF THE AVERAGE MOLYBDENUM-CARBON(CARBONYL GROUP) DISTANCES IN SOME MOLYBDENUM CARBONYL COMPLEXES

Compounds	Average Mo-C (Å)	Ref.
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Mo <sub>2</sub> H[P(CH <sub>3</sub> ) <sub>2</sub> ](CO) <sub>4</sub>	1.93(2)	8
[N(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Mo(CO) <sub>3</sub>	1.94(2)	14
C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>2</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COCH <sub>3</sub>	1.955(13)	11
C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	1.97(1)	13
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub>	1.97(2)	15
(i-C <sub>3</sub> H <sub>7</sub> )(CH <sub>3</sub> ) <sub>2</sub> C <sub>10</sub> H <sub>5</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	1.972(18)	16
C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> (CH <sub>2</sub> CO <sub>2</sub> H)	1.98(2)	17
C <sub>12</sub> H <sub>12</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	1.99(1)	18
[C <sub>10</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> CH <sub>3</sub> ] <sub>2</sub>	1.996(12)	12
C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>3</sub> F <sub>7</sub>	2.00(1)	9
(C <sub>2</sub> H <sub>5</sub> P) <sub>5</sub> Mo(CO) <sub>4</sub>	1.93(2)	19
	2.01(2)	
C <sub>7</sub> H <sub>7</sub> Mo(CO) <sub>2</sub> C <sub>6</sub> F <sub>5</sub>	2.017(9)	3
C <sub>7</sub> H <sub>7</sub> Mo(CO) <sub>3</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	2.032(12)	Present study
Mo(CO) <sub>6</sub>	2.06(2)	20

TABLE 5

## INTERMOLECULAR DISTANCES

Only the distances less than 3.2 Å involving heavy atom-heavy atom contacts and the distances less than 2.6 Å for heavy atom-hydrogen atom contacts are listed.

Atom 1-Atom 2	Position <sup>a</sup>	Distance (Å)
F(1)-O(2)	1	3.173(15)
F(1)-O(3)	1	3.195(15)
F(1)-C(9)	1	3.135(15)
F(1)-C(10)	1	3.131(15)
F(3)-C(2)	2	3.184(19)
F(4)-C(6)	3	3.156(20)
O(1)-O(2)	3	3.081(12)
O(1)-O(3)	4	3.117(17)
O(2)-C(3)	5	3.106(12)
O(2)-C(4)	5	3.197(12)
F(3)-H(2)	2	2.39
F(3)-H(5)	1	2.48
F(4)-H(6)	3	2.27
O(3)-H(2)	4	2.57

<sup>a</sup> Atom 1 is at  $x, y, z$  as given in Table 1 and atom 2 is in the position noted where the positions are: 1.  $\frac{1}{2}-x, -y, z-\frac{1}{2}$ ; 2.  $\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; 3.  $\frac{1}{2}-x, \frac{1}{2}+y, z$ ; 4.  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ; 5.  $\frac{1}{2}+x, y, \frac{1}{2}-z$ .

shortest Mo-C(ring) distances found in molybdenum-arene complexes indicates a stronger than normal interaction between the molybdenum atom and the C<sub>7</sub>H<sub>7</sub> ring. A similar effect is found in  $\pi$ -C<sub>7</sub>H<sub>7</sub>Mo(CO)<sub>2</sub>( $\sigma$ -C<sub>6</sub>F<sub>5</sub>) where the Mo-C(ring) distance was 2.316 Å and the Mo-C(carbonyl) distance was 2.017 Å. Although the two Mo-C(carbonyl) distances are not significantly different, the shorter distance in  $\pi$ -C<sub>7</sub>H<sub>7</sub>Mo-

$(\text{CO})_2(\sigma\text{-C}_6\text{F}_5)$  is easily rationalized on the basis of poorer back-donation to the  $\sigma\text{-C}_6\text{F}_5$  compared to a CO group. Therefore, we can generalize these observations by stating that neither the Mo-C(ring) or Mo-C(carbonyl) distances are expected to be constant but will reflect the strength and nature of the interaction of the other groups with the molybdenum atom. Whether in the case of  $\text{C}_7\text{H}_7$  complexes the stronger interaction is related to the ring size or to the formal positive charge on the ring can not be answered at this time.

The  $\text{BF}_4^-$  ion was not well defined, as indicated by the range of the B-F distances (1.21 to 1.30 Å) and F-B-F angles (96 to 118°). Unfortunately, the  $\text{BF}_4^-$  ion, the  $\text{ClO}_4^-$  ion and the  $\text{PF}_6^-$  ion are usually not well defined in a crystal structure determination, for reasons which are not completely clear. Although the majority of the intermolecular contacts given in Table 5 involve the fluorine atoms, the distances are all approximately the sum of the Van der Waals radii. The lack of any strong intermolecular attractions coupled with the approximately spherical nature of the  $\text{BF}_4^-$  ion may account for the lack of resolution of the ion in this case.

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